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54 **Glass powder adhesive sheet.**

57 A glass powder adhesive sheet used for a surface coating of inorganic structures comprising ceramics, metals, glasses, etc., a glazed ceramic substrate such as a substrate of electronic circuit, etc. or a heat-resistant label, etc., which comprises a glass powder molding comprising as main components, a glass powder and a resin binder, and an adhesive layer having a thermal decomposition initiation temperature higher than that of the resin binder, provided on the surface of the glass powder molding.

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GLASS POWDER ADHESIVE SHEET

FIELD OF THE INVENTION

5 The present invention relates to a glass powder adhesive sheet which is used for a surface coating of inorganic structures comprising ceramics, metals, glasses and the like, a glazed ceramic base plate such as an electronic circuit board, etc., or a heat-resistant label.

BACKGROUND OF THE INVENTION

10 Various surface coatings have heretofore been carried out for the purpose of improving characteristics of surface smoothness, abrasion resistance, corrosion resistance, surface hardness and the like, or for the purpose of an appearance decoration.

The surface coating methods include a vacuum evaporation method, sputtering method and the like. However, such methods are disadvantageous in that the equipment is expensive, it is difficult to form a thick coating layer, and so on.

20 Another method is a screen printing method wherein a paste comprising an inorganic powder and a resin binder as main components is coated and burned. However, due to the use of screen printing method, there are many disadvantages that the thickness of film formed at a time is limited, the operability is poor, printing on a curved surface is very difficult, and the like.

On the other hand, the glazed ceramic base plate is a ceramic base plate thinly coated with a uniformly molten glass, and is used for a hybrid IC, a thermal printer head, etc. A thin film circuit is formed by 25 forming a thin film on the glazed ceramic substrate by the vacuum evaporation method, sputtering method, etc. and patterning by photolithography. Accordingly, a smoothness of the surface becomes particularly important to improve a pattern accuracy of the circuit.

For the coating of glass on ceramic substrate, it has hitherto been most popular to coat a paste comprising a glass powder and a vehicle by means of the screen printing method.

30 However, this method has disadvantages that many times of printing must be carried out because it is difficult to form the necessary coating thickness at a time, the operability is poor, and the accuracy of the coating thickness is poor. Further, it has a disadvantage that a surface defect occurs because of entrapping bubbles at the time of printing.

In view of the above situation, a method for press-bonding a green sheet comprising a glass powder 35 and a binder as main components to a ceramic substrate is proposed as a method for easily producing a glazed ceramic substrate having excellent thickness accuracy as disclosed in JP-A-61-22682 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"). However, it has a problem that the bonding strength between the green sheet and the ceramic substrate is weak. In order to improve the bonding strength, it is considered to increase the amount of the binder added or lower T_g (glass transition temperature) of the binder. However, problems still arise that the former tends to form pinholes at burning due to lowering of packing density of glass powder and the latter lowers strength of the green sheet, becoming difficult to handle the sheet. Further, since the green sheet is press-bonded to the ceramic substrate with the binder, there has been a disadvantage that when the temperature is raised in the subsequent burning step, the bonding strength decreases before the binder disappears, and an edge 40 shrinkage of the glazing part occurs.

On the other hand, in transition of production system to multikind and small-quantity production, an identification label having necessary resistances such as heat-resistance, resistance to chemicals, etc. is demanded to control products, semi-fabricated products, parts, etc. Those resistances are particularly 45 demanded for the identification label to control glass products, metal products, sintered ceramic products, etc.

Heretofore, as an identification label which directly sticks to an article to be adhered and has a durability, heat resistance, resistance to chemicals, etc., labels comprising a substrate such as sintered ceramic, stainless steel, enameled ware, etc. have been known. However, such identification labels have

involved various disadvantages that the sticking by screwing takes much time, the sticking on a curved surface is difficult because of a lack of flexibility, and a formation of pattern having an excellent heat resistance is difficult in a job site, etc. As a result, it is difficult to expediently form the pattern in the job site, etc. to make an identification label.

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SUMMARY OF THE INVENTION

10 As a result of extensive investigations to overcome the above problems, it has been found that the problems of the conventional technique can be overcome by preparing a glass powder adhesive sheet.

The glass powder adhesive sheet according to the present invention comprises a glass powder molding comprising a glass powder, a resin binder and if necessary, inorganic powder and/or metal powder, and having provided on the surface thereof an adhesive layer having a thermal decomposition initiation
15 temperature higher than that of the resin binder.

DETAILED DESCRIPTION OF THE INVENTION

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When the inorganic structures are coated with the glass powder adhesive sheet having the above constitution of the present invention, a composition of the glass powder, the resin binder and if necessary, inorganic powder and/or metal powder is molded into a sheet form in advance, and such a sheet is used. Therefore, the thickness of coating layer can freely be chosen, thick film of coating layer can be easily
25 formed, and the thickness of the coating layer can be exactly defined. As a result, apparatuses required in the conventional vacuum evaporation method and sputtering method become unnecessary and also, there is no disadvantage due to the screen printing method, because of unnecessary thereof.

Further, lamination of the adhesive sheet can be carried out very easily and simply because it is conducted through an adhesive layer. In this case, a heat decomposition initiation temperature of the
30 adhesive is higher than that of the resin binder constituting the powder molding, and even if the resin binder in the powder molding decomposes in the burning step, the powder molding still adheres to an article to be coated and does not separate therefrom due to the presence of the adhesive. Consequently, a coating layer having excellent dimensional stability can be formed.

Furthermore, when the glazed ceramic substrate is prepared, the coating thickness can be controlled
35 accurately and easily, unlike that in the conventional printing methods, because the glass powder which had been made a sheet-form in advance is laminated to form the glass powder on the ceramic substrate. In addition, bubbles are not entrapped because defoaming can be fully made prior to the sheet formation, and the above glass powder molding is laminated simply by laminating the glass powder molding and the ceramic substrate and continuously guiding the laminate into rolling rolls, etc., and this laminating process
40 is far excellent in operability as compared with the conventional printing processes and can easily be carried out automatically. Accordingly, an automatic production line of the glazed ceramic substrate can be established by combining this lamination step with the subsequent burning step. In addition, when the glass powder molding is laminated on the ceramic substrate, since the adhesive layer having a thermal decomposition temperature higher than that of the resin binder constituting the glass powder molding is
45 used, the adhesive properties at room temperature are, of course, good to effect an easy laminating, and also even in the subsequent burning step, an excellent effect that a shrinkage of the glazed layer edge does not occur is exhibited because of still good adhesive properties even after the resin binder constituting the glass powder molding is decomposed.

When the powder adhesive sheet of the present invention is used as an identification label, the
50 identification label is obtained by temporarily attaching the above sheet or piece processed into a desired label shape, to a surface of a low adhesive base material prepared by coating a surface of the base material such as polyester film and kraft paper having a self-supporting property with a low adhesive compound such as silicone type resins and then forming a pattern of letter, figure or bar-code on the sheet with an ink for burning (e.g., JP-A-58-43486) which is different from a ground-color of the label. In this case, since the
55 adhesive layer having a thermal decomposition initiation temperature higher than that of the resin binder is used, even if the resin binder decomposes in the subsequent burning step after the identification label is stucked to an article to be adhered, good adhesive properties are still maintained and an effect that a slipping out of place and blister do not occur, is exhibited.

When the glass powder adhesive sheet of the present invention is used as the identification label, the embodiment that, for example, the formation of pattern with the ink for burning is carried out after the label is stuck to the article to be adhered or the identification is made without using the ink for burning but by using a difference of label shapes, a shaping holes or uneven surface on the label, or a sorting with label colors or colors of the article to be adhered and the label, should be included in the present invention.

The glass powders used in the present invention are conventional $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system, Pb-free $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ system and BaO-CaO-SiO_2 system colorless glasses, etc., and $\text{PbO-SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SnO}_2$ system colored glasses having a softening point of 300° to 1400°C and a particle size of 0.1 to 100 μm , preferably 0.5 to 30 μm .

Examples of the resin binder include synthetic polymers such as hydrocarbon resins, vinyl resin, acetal resin, acrylic resin, styrene resin, polyester resin, polyurethane resin, etc. or semisynthetic polymers such as cellulose resin, etc. Of those, the hydrocarbon resins, acrylic resin, acetal resin and cellulose resin are preferred from the standpoint of easy thermal decomposition, and the acrylic resin is particularly preferred.

The resin binder having a thermal decomposition initiation temperature of 100° to 350°C and a thermal decomposition termination temperature of 250° to 700°C is selected, and the amount added thereof varies depending upon a specific gravity and a particle size of the glass powder and the optionally added inorganic powder and/or metal powder, but the amount of 5 to 100 parts by weight per 100 parts by weight of the glass powder is preferred. If the amount is large, degassing is insufficient, resulting in foaming, and if the amount is small, the strength of the powder molding decreases and the operability deteriorates markedly.

The inorganic powder and/or metal powder are mainly used to improve surface characteristics in the case of the surface coating or glazed ceramic substrate, but in the case where the glass powder adhesive sheet is used as the identification label, it functions as a coloring agent which makes a contrast with the color of the ink for burning or the article to be colored, besides the improvement of surface characteristics.

The particle size of the powder is usually about 0.05 to 50 μm , preferably about 0.5 to 20 μm . The amount used thereof is about 1 to 50 parts by weight per 100 parts by weight of the glass powder.

Examples of the inorganic powder are SiC , SiN_4 , BN , Al_2O_3 , ZnO_2 , SiO_2 , TiO_2 , BaTiO_3 , MnO_2 , Cr_2O_3 , NiO_2 , CoO , Fe_2O_3 , Fe_3O_4 , etc., which can be used alone or mixtures thereof.

Examples of the metal powder are iron, chrome, copper, silver, gold, etc., which can be used alone or mixtures thereof.

In order to improve a uniform mixability of the glass powder, and inorganic powder and/or metal powder with the resin binder, a dispersing agent can also be used. Examples of the dispersing agent are various conventional surface active agents and the other aliphatic acid, aliphatic acid ester, fish oil, acrylic oligomer, etc. The amount of the dispersing agent used in this case is 0.01 to 10 parts by weight, preferably 0.1 to 2 parts by weight, per 100 parts by weight of sum of the glass powder and inorganic powder and/or metal powder.

When the powder molding is prepared, appropriate additives such as a solvent, a defoaming agent, etc. can be added to prepare a sheet-like molding by conventional doctor blade method, etc. That is, the powder molding having a good accuracy of thickness can be obtained by mixing a glass powder, a resin binder, a solvent, and, if necessary, inorganic powder and/or metal powder, a dispersing agent, a release agent, etc. in a ball mill and then casting the mixture with a doctor blade. Further, the bubbles in the sheet-like molding can be removed by sufficiently degassing a slurry before the casting. When this powder molding is prepared, an appropriate base film can be used to be the slurry casted thereon. The base film used in this case has a function to reinforce the powder molding and disappears in the subsequent burning step. Various synthetic resin films can be used as such a base film.

The adhesive layer is formed on the surface of the sheet-like glass powder molding (in the event that the molding is prepared by casting on a base film, on the surface having no film formation) by spraying, brushing or transferring the adhesive layer which has been previously formed on a low adhesive substrate, or directly coating an adhesive.

The material constituting the adhesive layer can be any materials having adhesive properties at room temperature or materials exhibiting adhesive properties by imparting external factors such as heat, water, solvent or the like if the material has a thermal decomposition initiation temperature of 100° to 350°C and thermal decomposition termination temperature of 250° to 750°C . Examples of the materials include polyethylene, ethylene copolymer, ethylene-propylene rubber, polyisobutylene, hydrocarbon resins such as petroleum resin, terpene resin, etc., acrylic resins such as polyacrylic ester, polymethacrylic ester, polyacrylamide, etc., diene resins such as polybutadiene, polyisoprene, etc., vinyl acetate, polyvinyl acetal resins, polyether resins, polyester resins, polyurethane resins, cellulose resins and the like. However, it is preferred from a standpoint of good operability to use materials having pressure-sensitive adhesive

properties at room temperature such as acrylic pressure-sensitive adhesives comprising a copolymer of (meth)acrylic acid ester and a vinyl monomer having a functional group copolymerizable with the ester; resin pressure-sensitive adhesives such as polyvinyl ether pressure-sensitive adhesive, etc.; or rubber pressure-sensitive adhesives such as neoprene rubber pressure-sensitive adhesive, isoprene pressure-sensitive adhesive, etc., alone or in combination with a hot-melt resin to decrease the adhesive properties.

In the combination of the adhesive with the above-described resin binder, it is necessary to combine in the manner such that the thermal decomposition initiation temperature of the adhesive becomes higher than that of the binder from the standpoints of dimensional stability and prevention of slipping out of position of the glass powder molding in the burning step. It is more desirable that the thermal decomposition initiation temperature difference should be at least 10°C, preferably 15°C.

The glass powder adhesive sheet thus prepared is adhered on a substance such as ceramics, glass, metal, etc. which is heat-resistant and does not deteriorate by heat in the burning step when the object is a surface coating; the sheet is adhered through the adhesive layer on a ceramic substrate such as alumina, beryllia, steatite, forsterite, zirconia, etc. when the object is to prepare the glazed ceramic substrate; and the glass powder adhesive sheet which is processed to be label-like and printed with an ink for burning, is stucked through the adhesive layer on an article when the object is the identification label.

The glass powder adhesive sheet stucked on the heat-resistant substance, ceramic substrate or object is heated up to the temperature higher than the softening point of the glass powder (usually 350 to 1,400°C) at a temperature raising rate of 5 to 30°C/min, whereby the resin binder is first decomposed and the adhesive layer is then decomposed to complete burning.

The glass powder adhesive sheet of the present invention enables structures made of ceramics, glass, metal, etc. to improve their characteristics such as surface smoothness, wear resistance, corrosion resistance, surface hardness, etc. when used as a surface coating material, and can be utilized for various parts such as electrical and electronic parts, automobile parts, mechanical parts, etc.

In the case of preparation of the glazed ceramic substrate, the thickness can be accurately controlled because of making a sheet-form in advance, and the defoaming can easily be carried out in advance before making a sheet-form. The adhesive properties are also excellent because the sheet is press-bonded to the substrate with the adhesive layer. Further, since the thermal decomposition initiation temperature of the adhesive layer is higher than that of the resin binder used for the glass powder molding, there are the following advantages in the subsequent burning step. Firstly, the resin binder in the glass powder molding has already decomposed to some extent at a temperature at which the adhesive begins to decompose by heat, and the glass powder molding is in the state having a gas permeability. Accordingly, since a decomposition gas generated by thermal decomposition of the adhesive can easily pass through the glass powder molding, no blister causes in the glass powder molding in the burning step, and a good smoothness and a good appearance can be obtained even after the burning step. Secondly, at a temperature at which the decomposition of the adhesive proceeds to lose an adhesive strength, the glass powder molding becomes powdery, and as a result, a shift of warpage, shrinkage, etc. in the layer of the glass powder molding arising when the resin binder remains therein, can be prevented. Accordingly, due to good adhesion between the glass powder and the substrate, shrinkage of the glazed layer can be prevented.

When the glass powder adhesive sheet of the present invention is used for the identification label, since the sheet can be adhered to an article in the unburned state, the sheet can be also easily adhered to a curved surface, and a product having an excellent durability, heat resistance and resistance to chemicals can be obtained. Further, since the thermal decomposition initiation temperature of the adhesive layer is higher than that of the organic resin binder, a slipping out of position and blister in the burning step do not take place.

The glass powder adhesive sheet can also be used for electronic parts such as circuit pattern, etc.

The present invention is now illustrated in detail by reference to the Examples and Comparative Examples, but it should be understood that the present invention is not deemed to be limited thereto. In these examples, all the parts are by weight.

EXAMPLE 1

SiO₂-CaO-BaO system glass powder having an average particle size of 11 μm was prepared.

100 Parts of the glass powder, 15 parts of a copolymer of butyl acrylate, methyl methacrylate and methacrylamide (60:35:5, thermal decomposition initiation temperature: 160°C, thermal decomposition termination temperature: 560°C), 1 part of oleic acid as a dispersing agent, 24 parts of toluene and 16 parts

of methyl ethyl ketone were mixed in a ball mill at room temperature, and the mixture was casted on a polyester film (thickness: 75 μm) using a doctor blade to obtain a powder sheet having a thickness of 100 μm . A 10 μm thick pressure-sensitive adhesive mainly composed of 2-ethylhexyl acrylate copolymer was laminated thereon. The composition of the pressure-sensitive adhesive was a mixture of butyl acrylate and acrylic acid (100:5) and had a thermal decomposition initiation temperature of 250°C and a thermal decomposition termination temperature of 590°C.

The above powder sheet coated with the adhesive was adhered on a ceramic molding comprising silicon nitride, and after binder-removal at 400°C for 30 minutes, the temperature of the ceramic molding was raised at the rate of 20°C/min. The temperature was maintained at 1000°C for 10 minutes to conduct burning. Upon measuring the thickness of the surface coated layer of the molding thus obtained, it was found that the layer had a good thickness accuracy of $65 \pm 2 \mu\text{m}$ and the surface smoothness was very good.

EXAMPLE 2

90 Parts of $\text{PbO-B}_2\text{O}_3$ system glass as a glass powder which contains 80 wt% of PbO and has an average particle size of 25 μm , 10 parts of alumina powder having an average particle size of 25 μm , 10 parts of isobutyl methacrylate as a resin binder having a thermal decomposition initiation temperature of 140°C and a thermal decomposition termination temperature of 340°C, 1 part of lauric acid as a dispersing agent and 35 parts of toluene as a plasticizer were mixed in a ball mill at room temperature, and the mixture was casted on a polyester film (thickness: 75 μm) using an applicator to obtain a powder sheet having a thickness of 80 μm . A 10 μm thick pressure-sensitive adhesive mainly composed of isoprene rubber was laminated on the powder sheet to obtain a powder tape sheet. The pressure-sensitive adhesive had a thermal decomposition initiation temperature of 200°C and a thermal decomposition termination temperature of 520°C.

The above powder tape sheet was adhered on a $\text{LiO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ system heat-resistant glass molding and the temperature of the glass molding was raised at the rate of 10°C/min. to burn it at 500°C for 10 minutes. A thickness accuracy of the surface coated layer thus obtained was good and there was no appearance troubles such as foaming, blister, etc.

EXAMPLE 3

A glazed ceramic substrate was prepared by the following method using a resin binder and a pressure-sensitive adhesive as shown in Table 1 below.

CaO-BaO-SiO_2 system glass having a softening point of 850°C and an average particle size of 11 μm was used as a glass powder.

100 Parts of the glass powder, 12 parts of a resin binder, 1 part of oleic acid as a dispersing agent, 24 parts of toluene and 16 parts of methyl ethyl ketone were mixed in a ball mill at room temperature, and the mixture was casted on a polyester film using a doctor blade to obtain a glass powder sheet having a thickness of 130 μm . A 20 μm thick pressure-sensitive adhesive was laminated on the above glass powder sheet. An alumina substrate having a purity of 96.0 % was used as a ceramic substrate. The glass powder sheet laminated with the adhesive was press-bonded on the alumina substrate. After binder-removal of the laminated sheet at 400°C for 60 minutes, the temperature of the alumina substrate was raised at the rate of 10°C/min. to burn it at 1270°C for 120 minutes, whereby the glazing was accomplished.

An appearance of the substrate thus obtained and an edge shrinkage were visually measured. The results are as shown in Table 1.

Table 1

Table 1					
	Resin binder		Pressure-sensitive adhesive		Measurement result
	Type	Thermal decomposition initiation temperature (°C)	Type	Thermal decomposition initiation temperature (°C)	
Example 3	Acrylic type A	160	Acrylic type B	180	Good Pinhole was found Edge shrinkage was found
Comparative Example 1	Acrylic type A	160	Acrylic type C	140	
Comparative Example 2	Acrylic type E	190	Acrylic type B	180	
Notes:					
1) Acrylic type A: Butyl acrylate/methyl methacrylate copolymer. (Thermal decomposition termination temperature: 580 °C)					
2) Acrylic type B: A mixture of butyl acrylate/acrylic acid copolymer and a terpene phenol resin. (Thermal decomposition termination temperature: 635 °C)					
3) Acrylic type C: 2-Ethylhexy acrylate / acrylic acid / methacrylic acid / glycidyl methacrylate copolymer (Thermal decomposition termination temperature: 470 °C)					
4) Acrylic type E: A mixture of butyl acrylate/acrylic acid copolymer and phenolic resin. (Thermal decomposition termination temperature: 650 °C)					

COMPARATIVE EXAMPLES 1 TO 2

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Example 3 was followed except for using the components shown in Table 1 above. The results are also shown in Table 1.

From the results shown in the above Table 1, it is found that the glazed ceramic substrate having a good appearance, a good surface smoothness and no edge shrinkage can be obtained only when the laminating was carried out using the pressure-sensitive adhesive having a thermal decomposition initiation temperature higher than that of the resin binder constituting the glass powder sheet.

EXAMPLE 4

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To 85 parts of $\text{PbO-B}_2\text{O}_3\text{-SiO}_2$ system glass powder having an average particle size of 11 μm and 15 parts of ZrO_2 powder, were added 20 parts of isobutyl acrylate having a thermal decomposition initiation temperature of 140°C and a thermal decomposition termination temperature of 340°C, 1 part of lauric acid and 42 parts of toluene as a dispersing agent, and the mixture was uniformly mixed in a ball mill at room temperature. The mixture was coated on a polyester film (thickness: 75 μm) using a doctor blade to obtain a powder sheet having a thickness of 60 μm .

A butyl acrylate/acrylic acid copolymer (Thermal decomposition initiation temperature: 250°C, Thermal decomposition termination temperature: 590°C) was laminated in a thickness of 20 μm on the opposite surface of the powder sheet film.

On the other hand, 30 parts of the above glass powder, 20 parts of chrome composition black pigment, 50 parts of butyl acrylate and 100 parts of toluene were uniformly mixed to prepare an ink for burning. Bar-code printing was made on a label material produced by processing the above glass powder adhesive sheet, by means of a screen printer using the ink for burning.

The identification label thus printed was adhered on the glass powder molding and the temperature of the molding was raised at the rate of 10°C/min. to burn it at 540°C for 30 minutes. The product showed the black bar-code clearly on a whitish ground and also showed no foaming, slipping out of position or crazing.

While the invention has been described in detail and with reference to specific embodiment thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

Claims

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1. A glass powder adhesive sheet comprising

a glass powder molding which comprises as main components, a glass powder and a resin binder, and an adhesive layer having a thermal decomposition initiation temperature higher than that of said resin binder, provided on the surface of the glass powder molding.

2. A glass powder adhesive sheet as claimed in Claim 1, wherein the glass powder has a softening point of 300°C to 1400°C.

3. A glass powder adhesive sheet as claimed in Claim 1, wherein the resin binder has a thermal decomposition initiation temperature of 100°C to 350°C.

4. A glass powder adhesive sheet as claimed in Claim 1, wherein the adhesive layer has a thermal decomposition initiation temperature of 100°C to 350°C.

5. A glass powder adhesive sheet as claimed in Claim 1, wherein difference between the thermal decomposition initiation temperature of the adhesive layer and that of the resin binder is at least 10°C.

6. A glass powder adhesive sheet as claimed in Claim 1, wherein the adhesive layer exhibits adhesive properties by receiving external factors.

7. A glass powder adhesive sheet as claimed in Claim 1, wherein a low adhesive substrate having a self-supporting property is temporarily provided on the surface of the adhesive layer.

8. A glass powder adhesive sheet as claimed in Claim 1, wherein the glass powder molding further comprises inorganic powder and/or metal powder.

9. A glass powder adhesive sheet as claimed in Claim 8, wherein the glass powder has a softening point of 300° to 1400° C.

10. A glass powder adhesive sheet as claimed in Claim 8, wherein the resin binder has a thermal decomposition initiation temperature of 100° to 350° C.

5 11. A glass powder adhesive sheet as claimed in Claim 8, wherein the adhesive layer has a thermal decomposition initiation temperature of 100° to 350° C.

12. A glass powder adhesive sheet as claimed in Claim 8, wherein difference between the thermal decomposition initiation temperature of the adhesive layer and that of the resin binder is at least 10° C.

13. A glass powder adhesive sheet as claimed in Claim 8, wherein the adhesive layer exhibits adhesive properties by receiving external factors.

10 14. A glass powder adhesive sheet as claimed in Claim 8, wherein a low adhesive substrate having a self-supporting property is temporarily provided on the surface of the adhesive layer.

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